

Origin of chert breccia at the unconformity between Precambrian Sirban Limestone and Paleogene Subathu Formation: evidence from Kalakot area, J&K Himalaya

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Petrographic and geochemical studies were carried on the chert breccia that lies between the Sirban Limestone of Precambrian age and early Paleogene Subathu Formation in the Kalakot section, Jammu and Kashmir, Northwestern Himalaya, India. The chert breccia is highly welded and more resistant to erosion than the underlying limestone. It consists predominantly of quartz occurring as angular to subangular fragments of varying sizes in a fine-grained matrix. Alkali feldspar (sanidine), biotite, iron oxides and zircon are present in minor amounts in the matrix. It has 90–91 wt% SiO₂, 3 wt% Al₂O₃, 0.25–0.42 wt% TiO₂ and 0.012 wt% P₂O₅. It has relatively higher concentrations (in ppm) of Zr (90–140), Y (20–23) and ΣREE (134–137), and significantly low contents of Sr (2–8) and Ba (3–38). Sirban Limestone consists of 46 wt% CaO, 12.91–13.34 wt% SiO₂ and 36 wt% loss on ignition. It has low concentrations of REE (ΣREE = 65–70 ppm) and relatively high content of Sr (525–534 ppm). The distinct mineralogy, texture and field features of the chert breccia are typical of a volcanic character, and the chemical composition is similar to that of a high-silica rhyolite.

Keywords: Chert breccia, geochemistry, high-silica rhyolite, limestone, volcanic origin.

THERE is an increasing interest in exploring and critically examining the late Cretaceous–early Paleogene stratigraphic record of the Himalayan Foreland Basin, to get valuable insights into the initial stage of collision of the Indian Plate with Eurasia. Early Paleogene sedimentary rocks belonging to Subathu Formation occur extensively in the foothills of the Northwestern Himalaya, in Jammu and Kashmir (J&K), Punjab, Himachal Pradesh and Uttarakhand (Figure 1)^{1–7}. They unconformably overlie rocks of different types and ages, and in Jammu region (J&K) Subathu beds rest on the Sirban Limestone of Precambrian age^{8–13}. Although tectonic setting of the region and biostratigraphic details of the Paleogene sequence have been studied by a number of researchers^{1,4,8–13}, little attention is being paid to understand their geochemical make-up. In Kalakot area of Rajauri District, J&K, about 4 m thick chert breccia crops out between the Sirban

Limestone (= Jammu Limestone/Vaishnodevi Limestone/Great Limestone) and the base of the Subathu Formation of Late Paleocene–Middle Eocene^{14–18}. Several researchers have highlighted the field characters of this (chert breccia) distinct and stratigraphically important litho-unit of the sequence^{14,15,17,18}. However, little is known about its petrographic features and geochemical characters, including absolute age, which are important to understand its origin, and in turn its relation (if any) to the India–Asia collision. Therefore, the aim of this contribution is to present results of mineralogical, textural and geochemical (including rare earth elements) study of the chert breccia and the underlying Sirban Limestone at Kalakot, and discuss its probable origin.

In the Jammu area, the Subathu Formation consisting dominantly of shallow marine sediments lies unconformably over the Sirban Limestone of Precambrian age^{15,17,18}. The unconformity is marked by the presence of a 4 m thick chert breccia in Kalakot area (Figure 2)^{15,17,18}. Since no index fossils have been found in the chert breccia, the Thanetian age assigned (based on foraminiferal assemblage) for the overlying basal interval of the Subathu Formation is also considered for the chert breccia^{17,19–21}. In fact, the chert breccia could have formed anytime between Precambrian and early Paleogene, and thus the assigned age is tenuous and equivocal. The chert breccia is overlain by silty carbonaceous shale of the basal Subathu Formation (Figure 2). The Sirban Limestone occurs as inliers, occupying the crestal part of anticlinal features. It is dark grey, hard, massive and siliceous. The chert breccia at Kalakot is hard, tough and compact, and breaks with conchoidal fracture, splintery when hammered and does not easily disintegrate. It is light brown to grey in colour. The chert breccia consists of angular to subangular, lensoid, elongate, centimetre to decimetre long fragments of quartz in a cherty matrix (Figure 3 *a* and *b*).

Based on upward fining nature of the fragments in chert breccia at Kalakot, Singh^{17,18} proposed a sedimentary origin for the same. He suggested that the fragments/phenocrysts present in the chert breccia were entirely composed of the basement rocks, i.e. the Sirban Limestone, and formed as a result of activation of growth fault during the India–Asia collision, which indicates that the chert breccia is a stratigraphic marker of the earliest collision between the Indian and Asian plates¹⁷. Occurrences of chert breccia, similar to the one at Kalakot have also been reported at similar stratigraphic level in Kanthan area in J&K²², and in Bidhalana and Pharat areas of Uttarakhand²³.

Ten representative bulk samples of chert breccia and Sirban Limestone were collected for laboratory studies. Thin sections were studied for texture and mineralogical composition. Mineral identification was confirmed by X-ray diffractometry. Major and trace elements were determined by XRF technique using pressed powder pellets

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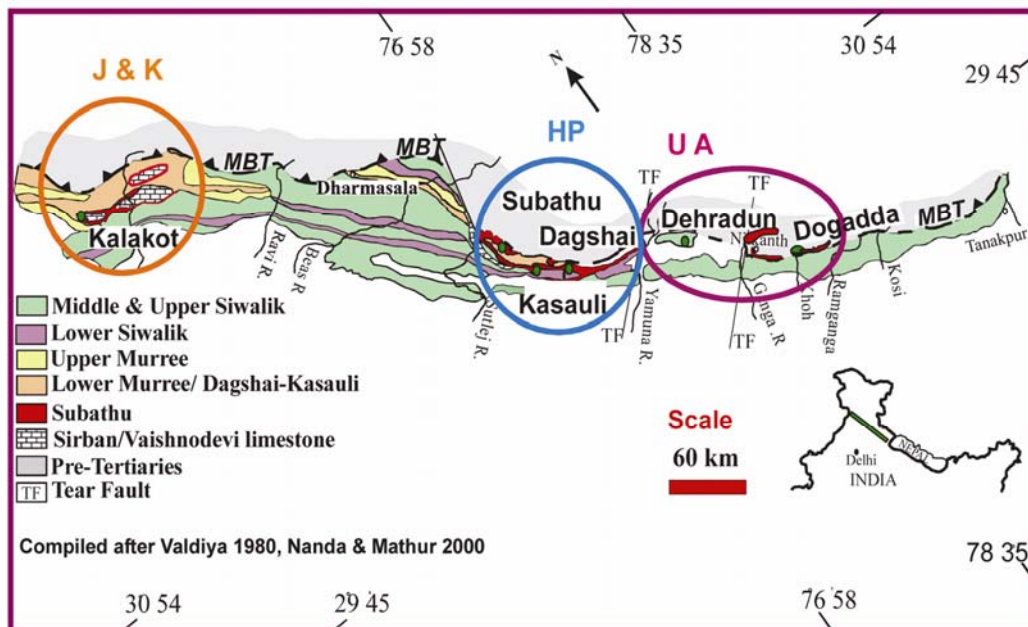


Figure 1. Geological map showing the occurrence of early Paleogene Subathu Formation in NW Himalaya^{2,7}. J&K, Jammu and Kashmir; HP, Himachal Pradesh and UA, Uttarakhand.

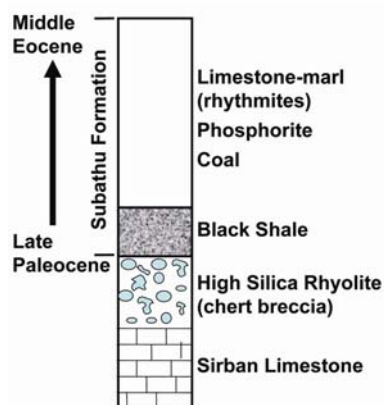


Figure 2. Simplified litholog of the Subathu Formation at Kalakot showing the stratigraphic position of chert breccia.

made from 5 g of sample. Carbonate and silicate fractions of Sirban Limestone were extracted by leaching 1 g of whole-rock sample powders with 1 N HCl. For REE estimation, 0.1 g of each sample powder split in PTFE beakers was digested using a 2 : 1 mixture of HF and HNO₃ at ~190°C under vapour saturation conditions for 24 h. After evaporation to incipient dryness and a second decomposition step with 5 ml of HClO₄ at 190°C in closed vessels, the residues were re-dissolved in 20 ml of 10% HNO₃ and made up to 100 ml volume with ultra-pure water. In these solutions REE were determined by ICP-MS. Reference standards [USGS (RGM-1 and G-2) and GSJ (JG-2, JLs-1 and JDo-1)] were used during the analysis, and the precision of major and trace element analyses is better than 2% and 5% respectively.

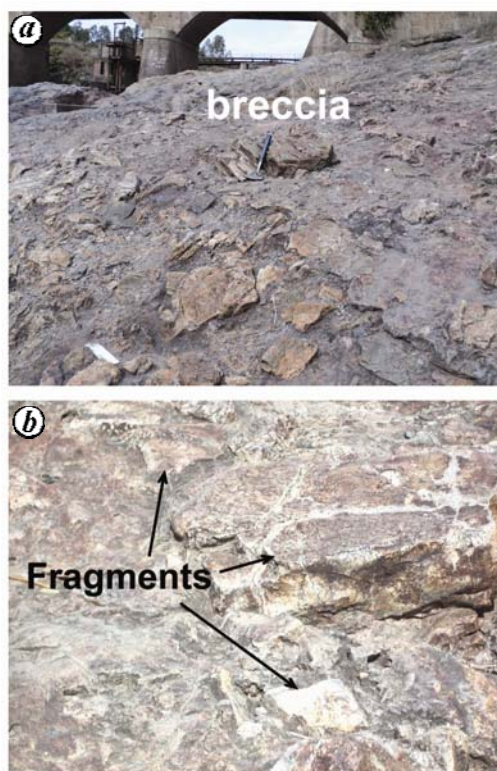


Figure 3. Field photographs of chert breccia at Kalakot showing (a) highly welded massive unit exposed at Kalakot village and (b) angular and lensoidal fragments.

The chert breccia at Kalakot consists predominantly of quartz followed by alkali-feldspar (sanidine), biotite, iron oxides and zircon in a fine-grained glassy matrix. Quartz occurs both as angular to subhedral phenocrysts and as

microcrystalline groundmass (Figure 4a). Preferred orientation of the fragments is lacking. Quartz grains show significant variation in size and shape and occasionally show resorbed/embayed margins (Figure 4b). Quartz phenocrysts have been fractured and shattered, and exhibit jigsaw-fit textures. Hexagonal bipyramidal, triangular, dagger, sickle and splintery-shaped morphologies are common in quartz grains (Figure 4c and d). Sanidine occurs as clear euhedral and subhedral elongate grains with simple Carlsbad twinning (Figure 4e) or with no twinning at all. Biotite occurs in hexagonal form (Figure 4f). Sirban Limestone consists dominantly of low Mg-calcite, and minor amounts of quartz as individual silt-sized grains (Figure 5).

Major and trace element (including REE) abundances in chert breccia (whole-rock) and Sirban Limestone (whole-rock, carbonate and silicate fractions of the Sirban Limestone) samples from Kalakot are given in Tables 1 and 2 respectively. REE concentrations in plots are normalized to CI-carbonaceous chondrite²⁴.

Whole-rock geochemical data of the chert breccia show very high SiO₂ (90–91 wt%), and low total alkali (Na₂O + K₂O = 0.31–0.74 wt%), low Al₂O₃ (3 wt%), TiO₂ (0.25–0.42 wt), MgO (0.2–1.73 wt%), CaO (0.13–0.14 wt%) and Fe₂O₃ (1.3–1.94 wt%). They are characterized by

enrichment in rare earth elements (Σ REE = 134–137 ppm), Zr (90–140 ppm) and Y (20–23 ppm) and depletion in large ion lithophile elements (Sr = 2–8 ppm and Ba = 3–38 ppm).

Table 1. Major (in wt%) and trace element (in ppm) composition of chert breccia and Sirban Limestone from Kalakot, J&K, NW Himalaya

	Chert breccia				Sirban Limestone		
	K1A	K1B	K1C	K1D	KO	KOA	KOB
SiO ₂	90.04	90.1	91.0	91.0	13.34	12.91	12.51
TiO ₂	0.26	0.25	0.42	0.35	0.151	0.142	0.144
Al ₂ O ₃	3.01	3.0	3.04	3.02	2.45	2.10	2.19
Fe ₂ O ₃	1.93	1.94	1.30	1.30	1.39	1.41	1.40
MnO	0.016	0.016	0.016	0.16	0.151	0.150	0.150
MgO	1.73	1.72	0.20	0.21	1.74	1.73	1.74
CaO	0.14	0.14	0.13	0.13	46.01	46.24	46.22
Na ₂ O	0.10	0.10	0.04	0.03	0.46	0.042	0.044
K ₂ O	0.21	0.22	0.70	0.70	0.22	0.22	0.22
P ₂ O ₅	0.012	0.012	0.01	0.012	0.033	0.04	0.04
LOI	1.46	1.45	2.0	1.62	35.97	36.0	36.0
Total	98.91	98.94	98.85	98.53	101.5	101	100.6
Sr	2	2	8	5	525	534	534
Sc	3	3	–	–	2.74	2.4	2.5
Co	21	20	23	22	3.28	2.74	2.70
Ni	32	31	10	11	–	–	–
Cu	27	25	24	25	–	–	–
Zn	83	79	–	–	–	–	–
Ga	3.1	3	5	4	–	–	–
Pb	50.4	48	100	60	–	–	–
Th	4	4	9	9	2.68	2.44	2.46
Rb	9.9	8	18	17	35.9	33.0	33.0
U	1.9	1.6	2.55	2	1.23	1.2	1.2
Y	22.5	23	20	21	11.44	10.73	10.74
Zr	91	90	140	107	–	–	–
Nb	6.4	6	8	7	3.28	2.99	3
V	23	22	48	31	35.01	34.60	34.5
Hf	1.45	1.5	–	–	1.1	0.98	1
Ba	38	37	3	5	–	–	–
Cr	70	73	80	67	–	–	–

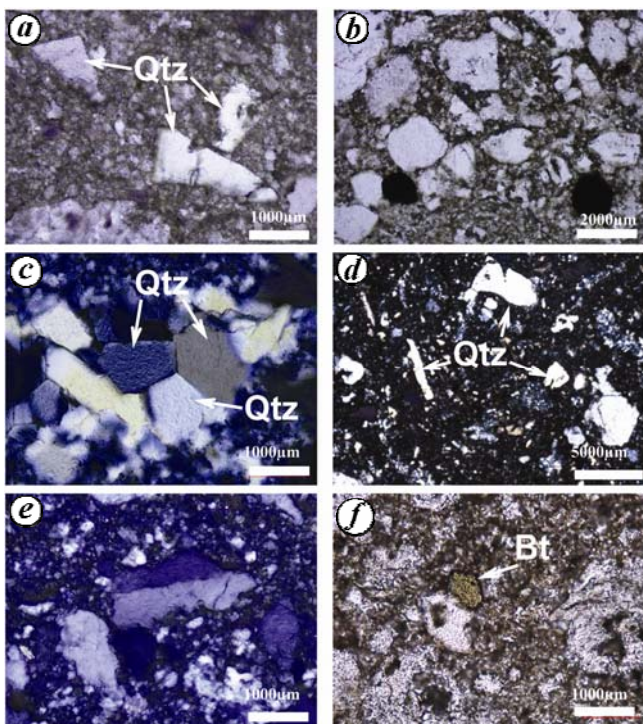


Figure 4. Photomicrographs of chert breccia at Kalakot showing (in crossed polarized light); a, Angular to dagger-shaped quartz in fine-grained siliceous ground mass; b, Phenocrysts of different shapes and sizes; c, Juxtaposed hexagonal bipyramidal quartz crystals; d, Sick-shaped and embayed quartz in fine-grained siliceous groundmass; e, Sanidine with Carlsbad twinning and f, Hexagonal biotite in fine-grained matrix.

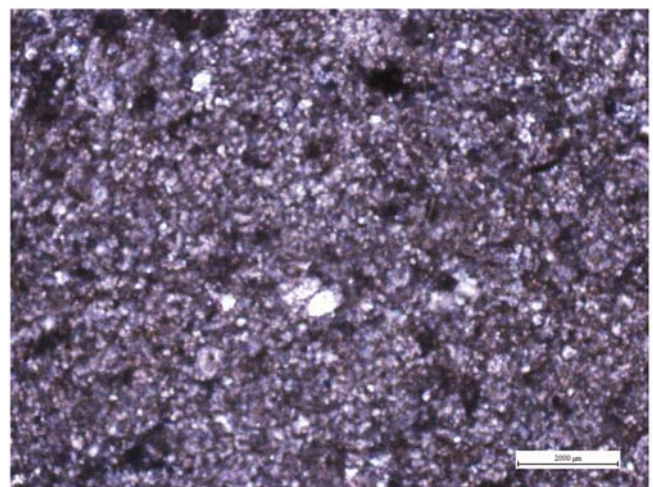


Figure 5. Photomicrograph of Sirban Limestone showing silt-sized quartz grains (white) in microcrystalline calcite groundmass; plane-polarized light.

Table 2. REE concentration (in ppm) in chert breccia and Sirban Limestone from Kalakot, J&K, NW Himalaya

	Chert breccia		Sirban Limestone						
	K1A	K1B	Sample # KO			Sample # KOA			NASC ³¹
			WR	SF	CF	WR	SF	CF	
La	25.13	25.1	13.87	31.75	6	13.37	27.112	4.526	32
Ce	45.98	45.9	25.62	54.97	13.85	24.40	48.969	10.409	73
Pr	7.36	7.37	3.28	5.03	1.73	3.01	4.114	1.313	7.9
Nd	35.37	35.32	14.11	17.53	9.02	13.48	13.415	6.508	33
Sm	6.78	6.73	3.71	2.31	2.07	3.30	1.588	1.543	5.7
Eu	1.39	1.40	0.88	0.45	0.60	0.88	0.340	0.422	1.24
Gd	4.98	4.97	2.55	2.02	1.80	2.43	1.566	1.287	5.2
Tb	0.84	0.85	0.42	0.41	0.31	0.40	0.281	0.219	0.85
Dy	3.66	3.65	2.41	2.85	1.62	2.22	2.021	1.144	5.8
Ho	0.71	0.71	0.43	0.70	0.31	0.43	0.524	0.214	1.04
Er	2.24	2.23	1.34	2.41	0.81	1.29	1.855	0.560	3.4
Tm	0.34	0.34	0.19	0.38	0.10	0.19	0.293	0.070	0.5
Yb	1.99	1.99	1.09	2.24	0.56	1.10	1.854	0.402	3.1
Lu	0.27	0.28	0.16	0.37	0.09	0.16	0.284	0.060	0.48
ΣREE	134.06	136.84	70.06	123.42	38.87	64.66	104.216	28.677	173
(La/Yb) _N	8.33	10.4	8.40	9.35	7.07	8.02	9.65	7.43	6.81
(La/Sm) _N	2.25	2.27	2.27	8.37	1.76	2.46	10.40	1.78	3.42

WR, Whole-rock; SF, silicate fraction, and CF, carbonate fraction; NASC, North American Shale Composite.

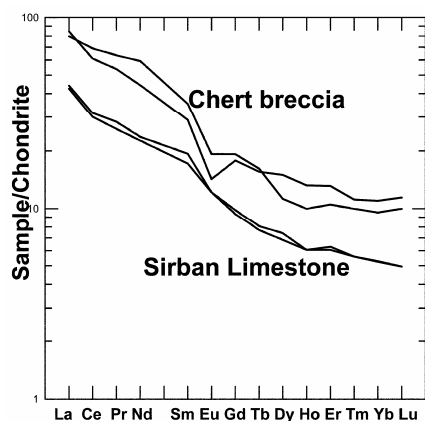


Figure 6. Chondrite-normalized REE patterns of chert breccia and Sirban Limestone.

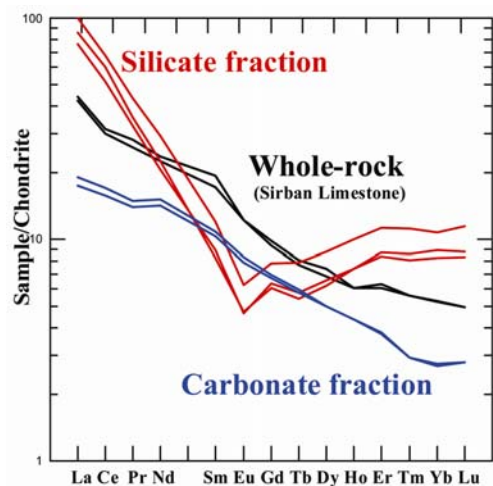


Figure 7. Chondrite-normalized REE patterns of silicate, carbonate as well as whole-rock of Sirban Limestone and chert breccia.

The Sirban Limestone consists dominantly of CaO (46.0 wt%) and SiO₂ (12.51–13.34 wt%) and high loss on ignition values (36 wt%). It has 525–534 ppm Sr and 1500 ppm Mn. It has low abundances of MgO (1.74 wt%) and REE (ΣREE = 64.66–70.06 ppm).

The chert breccia has much higher REE abundances compared to the Sirban Limestone (Table 2, Figure 6), and lower REE content compared to the average shale, i.e. North American Shale Composite (Table 2). The silicate fraction of the Sirban Limestone has much higher REE content (ΣREE = 104.2–123.4 ppm) than the carbonate fraction (ΣREE = 28.67–38.87 ppm; Table 2 and Figure 7).

The chondrite-normalized REE patterns for chert breccia shown in Figure 6 display sloping LREE (La_n/Sm_n = 2.25–2.27) and relatively flat HREE trends, with a distinct negative Eu anomaly (Eu/Eu* = 0.51–0.69). These REE patterns are similar to those of silicic tuffs from Proterozoic Singhara basin, Chhattisgarh²⁵. The normalized REE patterns of Sirban Limestone (whole-rock) exhibit a progressive decreasing trend from La to Lu, without Eu anomaly. Carbonate fraction of the Sirban Limestone shows low REE content (ΣREE = 28.67–38.87 ppm), but its chondrite-normalized REE patterns are similar to those of the whole-rocks (Figure 7). In contrast, the silicate fraction of the Sirban Limestone has higher REE abundances (ΣREE = 104.2–123.4 ppm) compared to the whole-rock, but its chondrite-normalized REE patterns deviate considerably from the whole-rock (Figure 7). The light-REE of silicate fraction shows steep negative slopes (La_n/Sm_n = 8.3–10.4) and moderately positive slopes for the heavy-REE along with a negative Eu anomaly (Eu/Eu* = 0.65). These patterns are distinctly different

from those of terrigenous sediment or upper continental crust, but strikingly similar to REE pattern for the high-silica rhyolites reported elsewhere in the world^{25–28}.

Detailed petrography and geochemistry of chert breccia and Sirban Limestone at Kalakot has provided new insights into the origin of chert breccia. The presence of hexagonal bipyramidal quartz, a typical habit of high temperature quartz, indicates a volcanic source. In addition, occurrence of quartz phenocrysts of different shapes and sizes with no preferred orientation; presence of high-temperature alkali-feldspar and hexagonal biotite, and grains with distinctive volcanic features like perfect crystal faces, embayments, skeletal grains and rounded fractures all support volcanic origin.

Thus the chert breccia at the top of Sirban Limestone at Kalakot displays field, mineralogical, textural and geochemical characteristics typical of a rhyolitic tuff breccia, as opposed to sedimentary chert breccia suggested by earlier workers^{17,18}.

Interestingly, occurrence of rhyolitic and agglomeratic breccia similar to the one at Kalakot has also been reported at similar stratigraphic level in Kanthan area, J&K, about 50 km east of Kalakot²². Silicic tuffs with 90 wt% SiO₂ and REE abundances, including immobile element ratios similar to the Kalakot breccia have been reported in Proterozoic Singhara basin in Chhattisgarh²⁵. If chert breccia at Kalakot is formed by silicification of Sirban Limestone as proposed^{17,18}, then higher abundances of REE in the chert breccia (134–137 ppm) compared to those in Sirban Limestone (65 ppm) does not support silicification modal. In fact, the silicification process decreases REE content and increases silica content to some extent. In addition, the chondrite-normalized REE patterns of silicate fraction of the Sirban Limestone show steep negative slopes for the light-REE and slightly positive slopes for heavy-REE (Figure 7) along with a negative Eu anomaly which is distinctly different from that of the terrigenous sediment such as shales and greywackes^{29,30}. In fact, these patterns are similar to the REE patterns reported for high-silica rhyolites^{25–28} and suggest an acidic-volcanic event coeval at least with the waning phase of deposition of the Sirban Limestone.

Therefore, the field, mineral, textural and geochemical data on the chert breccia at Kalakot suggest that it is a high-silica rhyolitic tuff breccia. The size and the angularity of the phenocrysts of the high-silica rhyolitic tuff breccia at Kalakot indicate that it is a product of an explosive volcanic eruption from a proximal source.

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Radioelemental characterization of fly ash from Chandrapur Super Thermal Power Station, Maharashtra, India

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Natural radioactivity due to the presence of ⁴⁰K, ²³⁸U and ²³²Th was measured in fly ash samples collected from economizer, aerator and electrostatic precipitator (EP) of the Chandrapur Super Thermal Power Station (CSTPS) using a NaI (TI)-based gamma ray

spectrometer. The study indicates an elevated concentration of these radionuclides, especially in the finer ash samples from EP, which may provide an exposure pathway through inhalation of airborne ashes and could probably cause severe environmental and human health problems. The present study gains significance as it provides the requisite basic data on the radionuclides concentration in fly ash from CSTPS for a detailed follow up of environmental monitoring and to formulate effective management strategies.

Keywords: Environmental monitoring, fly ash, radionuclides, thermal power plants.

COAL plays an increasingly important role to meet the ever-growing demand for energy, and coal-fired thermal power plants account for 54.3% (92,378.38 MW as on 31 December 2010) of the total electricity generation in India¹. This shall remain the mainstay to meet the additional capacity requirements in the future². But in this process of power generation, about 170 million tonnes (mt) of fly ash is produced annually in India alone, thus causing serious environmental problems³. Coal contains traces of naturally occurring radioactive elements like uranium, thorium and potassium, but their concentration depends on the composition and geological history of the coal⁴. Of the total 278,180 mt of coal deposits in India, approximately 276,810 mt comes from the Gondwana stratigraphic horizon and the rest from the Tertiary formations².

The Indian coal fields hold 77% of the sub-bituminous and bituminous coal reserves⁵, with high ash content and low calorific value⁶. Therefore, thermal power plants in India are designed to use these huge volumes of bituminous or sub-bituminous varieties having 30–40% ash content, which are otherwise unsuitable for metallurgical industries³. Upon combustion of coal, the nonvolatile products form ash particles that follow the air stream and eventually condense on the fly ash particles. It creates disequilibrium in the decay chain of parent radionuclides having different physical and chemical characteristics⁷. During the combustion process, the volume of coal is reduced by over 85%, which increases the concentration of ⁴⁰K, ²³²Th, ²³⁵U and ²³⁸U originally present in the coal⁸. Although significant quantities of ash are retained by precipitators, radionuclides such as uranium tend to concentrate on the tiny glass spheres that make up the bulk of fly ash. This uranium is released to the atmosphere with the escaping fly ash, at about 1.0% of the original amount⁹. The retained ash is enriched in uranium several times over the original uranium concentration in the coal^{10,11}.

Even though coal-fired power plants throughout the world are the major contributors of radioactive materials released to the environment¹², they have been neglected as a radiation source for a long time. Of late, due to advancement in the scientific knowledge of the biological effects of radiation on human beings^{13,14}, research activities are focused on increased concentration of naturally

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